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Bulletin of Spectrum Analysis

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INTRODUCTION.

The development of spectrum analysis and, in particular, of quantitative spectrum analysis of metals and alloys, has recently been very rapid. We have thought that the most convenient way of keeping our clients and enquirers informed of the new variations of technique brought forward from time to time would be the issue of this Bulletin. Our technical staff will be pleased to send further particulars concerning any of the methods described, or to quote for the additions to the standard spectrographic outfit for metallurgy described on page 8 of our booklet "Spectrographic Outfits for Metallurgical Analyses," to enable any of the methods to be employed.

The Bulletin will supplement the above-mentioned "Spectrographic Outfits" during the interval between successive editions of the latter. Such matter from the Bulletin as proves of durable worth will be transferred from time to time to "Spectrographic Outfits" or to other appropriate publications of the firm. Those interested in the history of practical spectrum analysis prior to September 1927 may consult "Two Lectures on the Development of the present position of Chemical Analysis by Emission Spectra," by F. Twyman, F.R.S. (Adam Hilger, Ltd., 1924, 2s. 6d. nett., 2s. 9d. post free).

Choice of Spectrograph or Spectroscope. In the choice of a spectrograph or spectroscope, the prime essentials are a sufficient resolving power, and good definition. The first and chief difficulty in the identification of the metals, particularly when they are present as impurities in small quantities, lies in the masking of their lines owing to their proximity

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to the lines of the main substance or of other ingredients. See also pp. 7 to 8 of " Spectrographic Outfits for Metallurgical Analyses " and p. 2 of " Applications of the Wavelength Spectrometer to Chemical Analysis." (Post free on request.)

THE QUANTITATIVE DETERMINATION OF IMPURITIES IN METALS AND ALLOYS BY MEANS OF THE QUARTZ SPECTROGRAPH AND LOGARITHMIC SECTOR PHOTOMETER.

The spectrographic estimation of small quantities of impurities in metals and alloys is based on the variations in the intensities of spectral lines due to these impurities, and several methods based on visual comparisons of these intensities have been used. Gerlach (*Zeits. f. anorg. und allg. Chemie*, **142**, p. 383, 1925) describes the internal standard method whereby the intensity of the impurity line is compared with that of a line due to the main constituent of the alloy. Where sufficient intensity standards are not available, a superimposed auxiliary spectrum can be used, the relative exposures of the two spectra being standardised (vide *Zeits. f. Metallkunde*, **20**, July 1928, p. 248). In this way the number of intensity standards can be artificially increased. In the spectrum of the spark the relative intensities of the lines emitted by neutral and ionised atoms are dependent on the amounts of capacity and self-inductance in the circuit. Schweitzer (*Zeits. f. anorg. und allg. Chemie*, **164**, 1927, p. 127) has investigated the effect of varying the electrical conditions on the character of the spark spectrum and obtained pairs of lines the relative intensities of which are practically independent of the discharge conditions. Such lines he calls " homologous pairs " of lines. To standardise the application of this method the electrical conditions are regulated so that the arc line 3330·6 and the spark line 3352·3 of tin are equal in intensity. The equality of intensity of the pairs of lines, one due to the impurity and the other to the main metal, is then correlated with the percentage of impurity present.

The accuracy of the visual comparison of the intensities of the lines is limited however, and several attempts have been made to apply a simple means of photometry. T. R. Merton has applied to Spectrum lines the wedge method originated by Mees[1] in which the lines are made to diminish

[1] *The Photographic Journal*, Jan. 1908.

in intensity along their length by placing a neutral wedge in front of the spectrograph slit. A considerable amount of experimental work has been carried out on this method of photometry.

(T. R. Merton. *Proc. Roy. Soc.* A. **92**. p. 322. 1916.
113. p. 697. 1927.

J. W. Nicholson and T. R. Merton.
Phil. Trans. A. **216**. p. 459. 1916.
217. p. 237. 1917.
220. p. 137. 1920. etc.)

The length of the line then gives a quantitative indication of its intensity. On account of the gradual decrease in intensity of the line the exact determination of the end of the line presents some difficulties, but with suitable plates and routine of development considerable accuracy is attainable.

W. H. J. Childs ("Some Methods of Estimating the Intensities of Spectral Lines"—*Proc. Phys. Soc.*, 70, April 1928, pp. 132-147) describes experiments made with a toothed wheel and also a cam driven shutter, which when placed in front of the spectrograph slit varied the time of exposure along the length of the slit.

The application of a similar method of spectrographic analysis is described by G. Scheibe and A. Neuhäusser ("Die Schnellbestimmung von Legierungsbestandteilen in Eisen durch quantitative Emissionspektralanalyse") in the *Zeitschrift für angewandte Chemie* (No. 45, Nov. 1928, p. 1218). The authors describe a comparatively simple method of photometry and have investigated the sensitivity and reproducibility of the method. A few examples, of technical interest, are given by way of illustration.

The following description is abstracted from the paper of Scheibe and Neuhäusser cited above. A sector is used whose aperture decreases in a logarithmic function, and the source of light is focussed on the spectrograph slit through this sector. The "blackening curve" of the photographic plate is also logarithmic and hence the length of the lines is somewhat proportional to the intensity.*

* The Abstractor is unable to agree with the statements in the paper represented by the passages marked with an asterisk on this and the next pages. Further, the method adopted by the authors of applying to metallurgical analyses the principles of wedge spectrography appears rather more complicated than need be.

None the less, the method seems likely to prove very valuable. It is being carefully investigated in the Hilger laboratories, and so far as the work has proceeded it confirms the estimate of accuracy given by Scheibe and Neuhäusser.

The appearance of the spectrum is similar to that obtained by the wedge methods of Merton, *i.e.* the lines gradually weaken in intensity along their length and finally disappear.

It is shown that for a wide range from under-exposure to over-exposure the ratio of the lengths of the lines (obtained by the sector method) remains constant.* The following data are given in support of this:

INTENSITY RATIOS OF THE LINES Sn. 2850 6
Pb. 2833·1

Atomic %	Length of Tin line. 1/10 m.m.	Length of Lead line. 1/10 m.m.	Ratio Sn/Pb.	Mean Value.	Exposure Secs.
3·0	30	24	1·25		5
	37	30	1·23	1·23	10
	43	35	1·23		20
	47	40	1·17	too long exposure.	40
2·0	36	27	1·30		5
	41	31	1·32	1·31	10
	43	33	1·30		20
	46	40	1·15	too long exposure.	40
1·3	30	22	1·36		5
	40	30	1·33	1·34	10
	40	30	1·33		20
	45	33	1·36		40
1·0	35	24	1·45		5
	41	28	1·46	1·45	10
	42	29	1·44		20
	45	31	1·45		40
0·8	37	25	1·48		5
	43	29	1·48	1·49	10
	45	30	1·50		20
	45	30	1·50		40
0·1	30	11	2·72		5
	43	16	2·70	2·71	10
	45	20	2·25	too long	20
	45	25	1·80	exposure.	40

For the ratio 1 the intensities of the two lines are equal. If the value of the ratio is much greater than 1, then on account of the complicated

law of blackening of the photographic plate, it does not follow that the ratio of the lengths of the lines is the same as the ratio of the intensities.* Nevertheless the number obtained is useful for comparative measurements.

A few pairs of lines for the system lead in tin as investigated by Schweitzer (loc. cit.) were studied with regard to the relation between intensity ratios and concentration of lead. The discharge conditions were first standardised by means of the spark line 3352·3 and the arc line 3330·6 of tin and further refined by means of the logarithmic sector.

The following pairs of lines were investigated :—

λ Pb.	λ Sn.	Equality of intensity is obtained with :
2833·1	2850·6	
2663·2	2661·3	10 atomic % Pb.
2614·2	2594·4	2 ,,
2823·2	2785·0	1·1 ,,
2873·3	2785·0	0·6 ,,

The curves reproduced, showing the relation between the intensity ratio and the concentration, indicate what may be generally expected from the spectrographic method. The error of the results is stated not to exceed 5% of the intensity ratio. For high percentage contents, where the curve becomes rapidly steep the error in the determination of an impurity content is comparatively large, while for small percentages it is much reduced. In many cases it was found that the percentage error of the total impurity content was almost constant over a fairly large range. In contrast to this, the absolute amount of the error frequently remains constant in a chemical analysis so that small percentage contents can be determined with much less accuracy.

The superiority of this method of photometry with the logarithmic sector over purely visual estimations of the equality of intensity of these pairs of lines is shown by the fact that the percentage content for which Schweitzer's equalities of intensity were obtained are not always in sufficient agreement with Scheibe's and Neuhäusser's results. This indicates the necessity, for accurate work, of using this photometric method, which requires no extension in the time occupied in making the analysis.

Experiments were made on the determination of Silicon and Manganese in Iron, these being of technical interest. Although difficulties were anticipated on account of the complex nature of the iron spectrum, it is

shown that the method is readily applied. The following pairs of lines were employed :—

IRON SILICON ALLOYS.

λ Si.	λ Fe.	Equality of intensity is obtained with :
2881·6	2880·8	1· 2% Si (by weight)
2881·6	2926·6	0·88% Si ,, ,,
2524·1	2523·7	0·5% Si ,, ,,
2528·5	2522·9	3·74% Si ,, ,,
2506·9	2507·9	

IRON MANGANESE ALLOYS.

λ Mn.	λ Fe.
2949·2	2944·4
2939·3	2923·9
2933·1	2923·9
2886·7	2912·2

The greater the number of standard samples of known impurity content, the greater will be the accuracy of the curve obtained. It is observed that care should be taken on account of the fact that the chemical analysis of silicon in iron is only possible with a limited degree of accuracy.

Another source of error may arise from the use of plates of different spectral sensitivity, but this can be rendered negligible by the use of one standard make of plates.

Having established the value of this method, the authors then turned their attention to the selection of a suitable means of obtaining the spark. The effect of varying capacity and self-inductance is illustrated by means of empirically determined curves. Experiments were made with the following types of apparatus :—

1. Induction coil with various types of interrupters.
2. A.C. transformers.
3. Resonance transformers.

The induction coil gave an irregular discharge of feeble intensity, and although the resonance transformer gave a very intense and constant spark, the discharge was totally different from that obtained with the other types of apparatus. Moreover, the intensity ratios in the case of iron-silicon alloys were not sufficiently reproducible, possibly on account of the great heat developed in the electrodes (which causes melting of such metals as lead and tin). Hence the method adopted was that of the A.C. transformer.

All things considered, it is concluded that technical analyses can be carried out by means of this method in a comparatively short time, with the consumption of very little material and with sufficient accuracy. For the determination of silicon in iron, for example, the total time required for an analysis amounts to 15 to 20 minutes, and by analysing a series of samples this time can be considerably reduced.

It is claimed that the accuracy over the range 0·8% to 4% is ±0·1%, and under 0·8% it is still greater. Also by using further pairs of lines obtained at the same time the accuracy could be increased still further.

Similar investigations to those described above can be carried out by means of the Logarithmic Sector Photometer (Catalogue No. H 195),† and for most non-ferrous alloys the dispersion and resolution of the E. 316 † Medium Size Quartz Spectrograph are amply sufficient. For iron and its alloys it is preferable to use the larger E.1† model, on account of the complex nature of the iron spectrum. The plates which we have found most satisfactory are the Ilford Rapid Process Panchromatic. A standard A.C. transformer etc. are available for use with an A.C. supply. The measurement of the lengths of the spectrum lines can be very accurately and conveniently carried out with the Photomeasuring Micrometer L.1.† Full particulars of these accessories will be sent on application.

BARRATT'S METHOD AND APPARATUS FOR QUANTITATIVE SPECTRUM ANALYSIS OF METALS AND ALLOYS.

British Patent No. 320136/28.

(This description has been prepared by Mr. S. Barratt, of the Spectroscopic Dept., University College, London, the inventor of the method.)

This method, of which this is the first published account, is peculiarly successful in some cases where the amount of the metal estimated in an alloy is large. When this is the case other methods of quantitative spectrum analysis give results so greatly inferior in accuracy to the chemical ones that replacement of the latter by the former has, for the estimation of large percentages of alloy metal, rarely come seriously into consideration.

The principle usually employed in the published work on this subject has been the comparison of a spectrum photograph from the unknown with a series of spectrograms from a graded set of samples—the com-

(†*These numbers refer to the Publisher's Catalogue.*)

position being judged by matching or rough interpolation. This method suffers from two main defects :

(1) The necessity of maintaining a " library " of graded samples for each element and for each type of material in which it has to be estimated.

(2) The uncertainty of reproducing the electrical discharge conditions from one occasion to the next.

The second defect can occasionally be overcome by the provision of " internal standards,"† but the existence of suitable lines for this purpose is a matter of chance.

The new procedure, which is now in the course of development, depends upon the photometric comparison, visual or photographic, of one or more lines of the element when excited simultaneously in the " unknown " and in a standard comparison material (*e.g.* a sample of the pure element), under electrical conditions which are identical—or bear, at least, a definite relationship to each other.

In practice, the unknown and the standard are made into the poles of two spark gaps arranged electrically in series, so that fluctuations in the discharge must affect the intensity of the emission from each material simultaneously. The two spark-gaps are arranged on a common mount, so that it is easy to ensure that their lengths are equal, and that they do not move relatively to each other. The photometric comparison of the spectra may be made by using, for example, a Nutting photometer in conjunction with a constant deviation spectroscope. It is more convenient, however, to have a special photometer and spectroscope built together as a single unit.

In using this instrument, the first adjustment, made with the slit well opened, is to bring the two sparks into the optical axes of the two polariser systems. This can be followed by removing the eyepiece of the telescope, and adjusting the sparks until both images are central in the object lens. The eyepiece is then replaced, and the slit is closed, but not so far as for ordinary spectroscopic purposes, as it is much easier to match a " band " than a narrow line. The line is isolated in the field of view by the shutters in the eyepiece, and the two images are then ready for comparison by the photometer.

This is the form in which the apparatus has been employed up to the present. The principle can be extended to the ultra-violet by using a Hilger sector photometer together with a quartz spectrograph, the sectors

† The method proposed by Gerlach, in which the line of an impurity is compared with a neighbouring line of the main substance (see reference on page 2, also Technical Publication No. 79, Class E, Institute of Metals Division, Amer. Inst. Mining and Metallurgical Engineers).

being adjusted until the lines of the element under estimation are photographically of the same intensity in the "unknown" and in the standard.

For the purposes of analysis, measurements of relative intensity made by any of the preceding systems have next to be turned into estimates of relative composition. Since, as yet, we have no comprehensive knowledge of general principles according to which intensities vary with composition (the investigation of this problem is an attractive application of the apparatus), the composition estimates must be made empirically. A series of samples covering the required composition range are first compared against each other, or against a 100% sample of the element, and an experimental curve is drawn showing the change of intensity with composition. It is convenient, in many cases, to plot the logarithms rather than these quantities themselves; as curves so plotted are readable, at all their points, with an accuracy proportional to the accuracy of the corresponding spectroscopic observation. The unknown is then compared with a standard chosen for convenience and the estimate of its composition can be read from the curve. Once the curve has been constructed, the graded series of samples is not required for further analysis, one or two standard comparison samples sufficing.

The conditions for the most successful application of the method to each individual problem have still to be determined. The reproducibility of results, within the observational error has, however, been established. Two alloys, for example, will always give the same relative intensities in their spectra, when suitable precautions are taken. The optical arrangements permit of an accuracy of 1% in a determination,† *i.e.* it would be expected that in a substance containing a percentage A, the determination would be made to about one-hundredth part of A. But limitations of the method are sometimes fixed, not by the optical system, or by failure of the method of balancing out the fluctuations of the discharge, but by the shapes of the composition-intensity curves.

The results so far obtained indicate that for small percentages of a given alloy constituent, the log(Intensity)—log(Composition) curve is either actually, or very nearly, a straight line. At higher concentrations, say above 10%, the curve is characteristic of the alloy. For some alloys (*e.g.* Zn-Cd) over the whole range (100% Cd—100% Zn) the curve is still a straight line (or nearly so). With other alloys (*e.g.* Cu in Ag), the intensity of the lines of one constituent remain constant over a wide range of composition (8%—50% Cu), below 8% the intensity giving a satisfactory measure of the copper content.

†This refers to the visual method—where photography has to be employed the accuracy is less.

The characteristics of these and other curves, and their interpretations, are in course of investigation, and the conclusions are as yet only tentative.

The points which must receive attention during measurements are :

1. The two gaps should be of equal length.
2. A standard length of gap should be used.
3. After the discharge is started, the intensities from some alloys change for a short " induction period " (if compared with 100% material). The length of this interval before steady readings are obtained is very soon found by a series of observations.
4. If an alloy, and not a pure metal, is used for comparison, its surface should be renewed before each analysis.

It must be understood, having in view the enormous variety of alloys whose spectroscopic analysis becomes practicable by this means, that a complete technique will take some time to perfect.

Another application of the double spark principle is also possible when a photometer is not available. The sparks are used as before, but in place of the single standard, a series of standards is introduced successively, and the intensities compared with that from the unknown, either visually or photographically, the images being brought into juxtaposition on the spectroscope slit by a biprism. This procedure is, of course, the old one, with the uncertainties due to the source removed, and the possibility of visual working superadded. The bringing of the lines into close juxtaposition also increases the accuracy of matching.

THE QUANTITATIVE SPECTROSCOPIC METHOD OF ANALYSIS OF OCCHIALINI.†

A. Occhialini (at the University of Genoa, Italy), is investigating a method of quantitative spectroscopic analysis which is based on the measurement of the lengths of the lines of the element sought, in the spark spectrum of the substance. Details of this method have been kindly communicated to us by the author.

It is found that the whole of the spark does not give out radiations characteristic of the more sparsely distributed elements in a sample, but only those parts of it adjacent to one or other of the electrodes, if the capacity in the circuit be suitably adjusted. Furthermore, it is stated by Occhialini that the extent of the length of the spark over which these radiations are emitted, bears a relation to the resistance in the spark

† This brief account is published with the kind permission of Prof. Occhialini. It is intended to publish further details later.

circuit and the concentration of the element in the substance. The determination to be made, then, is of the limiting position in the source at which a given line disappears from the spectrum. By analogy with the work of Lockyer (who first noticed the variations in length of the lines produced in his spectrograph when a spherical condenser was used) we may speak of the " length of the line " as the distance from one pole of the source over which it is emitted.

By means of an achromatic lens, mounted upon a slide whose position is determined by a precise screw motion, an image of the spark (between horizontal electrodes) is projected on to the spectroscope slit. The image is moved across the slit by means of the screw motion until the image of the edge of one electrode coincides with the slit. Then the lens is slowly moved back until the spectrum line under observation disappears from view. The motion of the lens is then related to the length of line, the resistance in the circuit and the quantity of the substance present. Curves relating these quantities can be constructed readily and from them the unknown data can be deduced.

This method is applicable to both low and high concentrations. For high concentrations smaller capacity is used than for small concentrations in order to obtain lines of suitable length for measurement. The complete curve for a single concentration requires only half an hour for its investigation.

Experiments are now in progress to determine whether the ratio of the lengths of two lines due to different constituents of an alloy or solution depends only on the relative concentrations of these constituents, and not on the conditions of the discharge. If this should be the case, this ratio would form the basis for absolute determinations of the constituents.

The following observations have been made, which are of more theoretical interest :—

1. All the lines of the same order of ionisation of an element are related to a single curve.
2. The ratio of the lengths of the components of doublets and triplets of the same series is constant.
3. The length of an arc line is not influenced by the polarity of the electrode.
4. The length of a spark line (*e.g.* 4481 of Magnesium) is greater when the electrode is positive than when it is negative.

(The last two results are evidence of the fact that the atoms which emit the arc lines are neutral, while those which emit the spark lines are positively charged.)

THE QUANTITATIVE ANALYSIS OF SOLUTIONS BY MEANS OF FLAME SPECTRA.

A comprehensive investigation of the application of flame spectra to the determination of small quantities of Potassium, Magnesium and Copper in solutions has been made by H. Lundegardh ("Investigations on Quantitative Spectral Analysis"—*Arkiv for Kemi, Mineralogi och Geologi*, 10 A. No. 1, Oct. 1928).

The nozzle spraying apparatus employed was a modified form of that devised by Gouy (*Ann. Chim. et Phys.*, 18, p. 5, 1879). Pure acetylene gas was used for the flame, and the spectra were photographed with a Quartz Spectrograph. The spectra of several standard solutions were photographed on the same plate as those of the solutions to be tested. The intensities of the lines were measured with a thermo-electric photometer, scale readings being obtained with a Hartmann and Braun galvanometer.

Extensive tables of numerical data are given, and the following problems were investigated :

1. Accuracy and Sensitivity of the method.
2. Influence of variations in gas and air pressure.
3. Influence of anions and kations in the solution.
4. Total error of analysis and corrections.

The method was developed to supply the need for a rapid micro-method (especially for potassium) for chemical problems in physiology and agriculture. It is claimed that the method is more accurate than previously used micro-methods for potassium, magnesium and copper.

March 1929.—*Revised September* 1930.

BULLETIN No. 2 (published May 1930, 23 *pp.) can be obtained post free on request, and contains—*

A Summary, with references, of Applications of Quantitative Analysis with the Spectrograph,

Bibliography of Recent Papers on Spectrum Analysis,

Official Specifications for Lead, Copper, and Zinc,

Other information concerning Metallurgical Spectrum Analysis,

Physiological, Pathological, Toxicological and Pharmaceutical Applications of Spectrum Analysis

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